QUANTITATIVE INFRARED MULTICOMPONENT ANALYSIS OF MINERALS OCCURRING IN COAL

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INTRODUCTION

The recent development of a new low-temperature ashing technique (12) for obtaining unaltered mineral matter from coal, combined with the extension of the mid-infrared region to 200 cm^{-1}, has shown clearly that infrared spectroscopy is a valuable tool for use in coal mineralogical studies (15). The direct infrared analysis of minerals in coal has been hindered previously by the broad background absorption of the coal itself (11) as shown in Figure 1, curve (b), coupled with the paucity and often nonspecificity of mineral absorption bands in the rock-salt region of 5000 to 650 cm^{-1}. However, when the coal substance, approximately 90% of the sample, is removed at low temperatures in an oxygen plasma (12), there remains unaltered mineral matter with an infrared spectrum exhibiting many diagnostic and analytically useful absorption bands as shown in Figure 1, curve (c). The disappearance of organic absorption bands indicates complete removal of the coal substance. The improved quality of the spectrum obtained on this enriched mineral matter has increased the possibilities for quantitative analysis. In this paper we describe the development of an infrared solid state quantitative analysis for five commonly occurring coal minerals--quartz, calcite, gypsum, pyrite, and kaolinite. The presence of many other minerals in coal in a wide range of concentrations has been shown (6, 9, 16, 28). However, those included in this analysis were selected on the basis of their frequency of occurrence and relative abundance in the coal samples examined in this laboratory. We anticipate that in this continuing broad program using infrared spectroscopy for coal mineralogical studies, qualitative and quantitative analysis can be developed for other minerals.

A large part of the published infrared data for minerals (1, 14, 30) and inorganic compounds (26) is limited to the rock-salt region of 5000 to 650 cm^{-1}. Recently, spectral data in the extended region of 650 to 400 cm^{-1} has been presented for some minerals (31, 37) and down to 240 cm^{-1} for some inorganic compounds (24, 25, 32, 38). However, these collections offer very few high-resolution spectra for naturally occurring minerals to 200 cm^{-1}. The published papers on quantitative infrared analysis of minerals have dealt with a single mineral or the detailed studies of sampling parameters, while very little has appeared on multicomponent mixtures (14, 23).

EXPERIMENTAL

Several specimens of each of the five minerals were obtained from different localities and their infrared spectra checked qualitatively for associated mineral contamination and phase purity by three means: common agreement of the spectra for samples from several sources, literature infrared data, and X-ray powder data. On the basis of this qualitative screening, two sources were

selected for detailed grinding studies in order to establish the infrared absorptivity calibration data. The mineral was placed with an agate ball into an agate vial, approximately one-third full, and ground mechanically in a Spex Mixer Mill. A sample was removed from the vial for infrared analysis at five-minute intervals with a five-minute cooling period. The grinding was continued until measured band absorptivities became constant, at which point a particle size determination was made using a Coulter Counter, Model A (Coulter Electronics). Pellets for the infrared analysis were prepared by weighing one milligram of the pregound mineral and 500 milligrams of cesium iodide powder (Harshaw, 100 to 325 mesh, median particle size 62 μ) on a microbalance and blending by hand for five minutes in a mullite mortar. This mixture was transferred quantitatively to a die and pressed into a pellet according to a triple press method (13). For this the pellet was placed under vacuum, pressed for five minutes at a pressure of 23,000 pounds total load, the pressure relaxed for five minutes, and the procedure repeated twice. The additional pressing steps presumably relieve the strain introduced by the original pressing. The resulting pellet of 0.80 by 13 mm was then scanned immediately on a Perkin-Elmer 621 infrared grating spectrophotometer purged with dry air.

Enriched mineral samples from coal were prepared by low-temperature oxidation at 145° C in an oxygen plasma using Tracerlab's Model LTA-600. Each of the five minerals was exposed to the same ashing conditions as the coal samples. There were no sample alterations, except for the partial dehydration of gypsum to the hemihydrate.

RESULTS AND DISCUSSION

Sampling Parameters

Tuddenham (35) has shown the application of the potassium bromide pellet method to mineral analysis and demonstrated its quantitative potentialities. Most infrared spectroscopists conclude that it is possible to achieve acceptable solid state analysis only with rigorously standardized conditions of sample preparation. The many difficulties encountered in quantitative solid phase spectroscopy have been reviewed by Duyckaerts (10), Kirkland (17), and Baker (5).

Particle Size. Probably the most important single physical factor to be considered in quantitative solid state spectroscopy is that of particle size. This problem has been investigated both theoretically and experimentally by several workers (10, 19, 34, 35). As particle size is reduced there is a reduction of light loss by reflection and scattering and the intensity of an absorption band increases from an apparent absorptivity to its true absorptivity value. Descriptions of this relationship between particle size and absorptivity for the mineral calcite has been given by Lejeune (19) and Duyckaerts (10) and for quartz by Tuddenham (35). Other workers have used the more empirical approach of relating infrared absorptivities to sample grinding time, which is proportional to particle size. The commonly used sedimentation technique for obtaining the required particle size of the sample, while applicable to single component samples, cannot be employed with multicomponent samples (14, 35) since this procedure leads to a differential separation of the individual components. The effects of particle size reduction can vary with different minerals and can vary for absorption bands of different intensities. Kirkland (17) has pointed out that the absorptivities of bands associated with crystallinity

can be more susceptible to particle size variations than those originating from functional group vibrations. These considerations necessitate a careful study of the effects of particle size on absorptivity for each band being considered for quantitative analysis. For this work the expedient method of studying absorptivity as a function of grinding time was chosen. If a strict grinding schedule is followed, particle size need only be determined on those samples ground for lengths of time necessary to produce constant absorptivity values. Thus, knowledge of particle size requirements for constant absorptivities is available with a minimum of effort. A typical example of such a grind study is shown in Figure 2 for the mineral pyrite. The data show that the apparent absorptivity becomes constant after a minimum grinding time and remains constant even with extended grinding and further particle size reduction. The minimum grinding time for a particular mineral can vary with the type of vial used and the amount of sample loaded into the vial. Grind studies on all five minerals reveal that at the minimum grind time, the mean particle size of the sample falls in the range of 4 to 13 microns. This fulfills the theoretical requirement for solid phase spectroscopy, that is, sample particle size should be less than the wavelength of the incident radiation, in order to minimize scattering, reflection, and the Christiansen effect.

While the absorptivities as determined for use in this analysis are constant, they are not necessarily maximum values. Particle size reduction of the cesium iodide matrix can cause band absorptivities to increase markedly. This effect was shown in a grind study in which preground kaolinite was added to samples of cesium iodide, also preground, but for different lengths of time. Each mixture was then hand blended to prepare a pellet according to the chosen procedure. Absorptivities for several kaolinite bands were seen to increase 30 to 50% when prepared with cesium iodide that had been ground for 20 minutes. True absorptivities could not be determined because, at a very fine particle size, cesium iodide pellets crumble. While not recommended for quantitative work, grinding samples for five minutes in a ball mill with cesium iodide is a good technique for improving the qualitative appearance of the spectrum; band resolution improves and background is considerably reduced. The relatively gentle grinding that the cesium iodide receives during the blending stage of pellet preparation reduces its particle size very little as shown by particle size determinations. Since quantitative accuracy is more a function of reproducibility rather than absolute measurement, the relatively simple and highly reproducible method of hand blending was chosen. An additional reason for selecting this method over the technique of mechanical blending in a ball mill is that the cesium iodide mixture packs in the vial and is not quantitatively recoverable.

Sample Alteration. Extensive grinding can cause polymorphic transformations or alteration of mineral composition. For example, Dachille (8) has shown that a few minutes grinding in a Wig-L-Bug with a metal vial and ball can transform calcite to the high-pressure phase of aragonite. He assigns this transformation to a pressure component in the mechanical action of the vibrator. Burns (7) also studied this calcite-aragonite transformation and found that it can occur by grinding at room temperature. Morris (27) found that vibrating for more than one minute in a stainless-steel Wig-L-Bug will cause dehydration of gypsum. Liberti (20) has reported destruction of the crystalline structure of quartz under certain grinding conditions. We have noted changes in the spectrum of kaolinite after it was subjected to severe grinding conditions. However, none of these

alterations were observed by using the chosen procedure, presumably due to the periodic cooling periods during grinding and to the use of an agate grinding ball mill. Since the density of agate is about one-third the density of stainless steel, there is less mechanical stress exerted on the sample in this vial. The absorptivity values of some absorption bands began to decrease with prolonged grinding, although no qualitative spectral changes occurred. Since some form of sample alteration occurred, these bands were not selected for use in the quantitative analysis.

Particle Distribution. If Beer's law is to be followed, all absorbances must show a linear dependence on effective concentration. The concentration is considered effective because the infrared beam does not completely cover the entire pellet in the instrument. The use of sample weight as a concentration factor thus requires a high degree of uniform dispersion, or a homogeneous mixture of sample and matrix. This can be achieved if particle size is small and if blending is thorough. In the instrument used, the infrared beam covers about 50% of the pellet area. As a test of the dispersion achieved with the chosen sample preparation technique, pellets of each of the five minerals were rotated systematically through 360° with scans taken at several settings. For all positions, the band intensities were identical, indicating that dispersion is adequate, and also that there are no polarization or orientation effects.

Choice of Matrix. Several salts were tested for use as a matrix. Cesium iodide appeared to be the best choice on the basis of its superior transparency at long wavelengths. The low background at shorter wavelengths due to scattering was not objectionable since most of the useful absorption bands for minerals are found at longer wavelengths. The triple press method reduced scattering at short wavelengths, often as much as 40% over single pressing. The over-all transmission of a blank cesium iodide pellet was acceptable, as shown in Figure 1, curve (a), and therefore no pellet was used in the reference beam. Although cesium iodide is slightly hygroscopic, there was less difficulty from water adsorption than is generally experienced using the more common potassium bromide matrix. While mechanical grinding of cesium iodide intensified the water absorption bands, hand blending produced no more than 0.02 absorbance units at the 3430 cm^{-1} OH stretching frequency. This behavior of cesium iodide has a decided advantage since coal minerals often have useful OH absorption bands.

The pellet thickness must be controlled in order to prevent interference or fringe patterns. In the longer wavelength region where the requirements for parallel pellet surfaces are relaxed, these fringe patterns can become quite pronounced on thin pellets. In order to eliminate this as a potential source of quantitative error, pellets at least 0.80 mm thick were used.

Other Parameters. There are other sampling problems sometimes encountered in solid state analysis. Among these is interaction of the sample with the matrix, believed to be negligible for the minerals analyzed here. A large refractive index difference between the sample and the dispersion medium can cause a pronounced Christiansen effect, characterized by the asymmetrical shape of an absorption band, and resulting in high light scattering which can introduce errors into quantitative measurements. However, the small particle size used should minimize any error arising from this effect. Departure from Beer's law is possible, but with the base line technique for absorbance measurements and with

controlled particle size, Beer's law was obeyed for concentration ranges of 0.02 to 0.2 wt-pct. One of the limitations in the quantitative analysis of minerals and inorganics is due to their inherently high band absorptivities. With intense absorption, only a very small amount of sample can be included in the pellet, so that the band will still be measurable, thus increasing weighing errors. However, reproducible results could be obtained with a microbalance and a large area of beam coverage of the pellet.

Qualitative Analysis

Since natural mineral specimens, which were used as standards in this analysis, often occur in polymorphic aggregations, it was necessary to determine the qualitative infrared spectral differences for polymorphs of each mineral. In the coal samples thus far investigated no polymorphic mixtures were encountered, although they can be expected. Table 1 lists the spectral data from this laboratory for each of the five minerals and some polymorphic forms.

Quartz. The two quartz samples used as standards, for which bands are presented in Table 1 and absorptivity data in Table 2, are both low-temperature α-quartz. This was established from differences shown in the infrared spectra of samples of polymorphs of crystalline silica in this laboratory, from literature data (21, 33, 39), and from X-ray powder data. The α-quartz form can be distinguished in the 650 to 200 cm^{-1} region from the polymorphic forms of α-tridymite and α- and β-cristobalite. Work remains to confirm the distinction of α-quartz from β-quartz and β-tridymite. The distinction of α-quartz from its crystalline polymorphs and other modifications of silica can be made by the highly unique bands at 256, 363, 388, and 688 cm^{-1}.

Calcite. The natural aggregation of calcite and its dimorph aragonite is common (3). Infrared literature data (2, 3) in the rock-salt region show that hexagonal calcite can be distinguished from orthorhombic aragonite. The data from our laboratory in Table 1 show the marked difference in their spectra and list the additional bands obtained for the region 650 to 200 cm^{-1}. Petrographic distinction between these two polymorphs is often inadequate as shown by the fact that three of our samples labeled aragonite were shown by infrared to be calcite. Adler (3) found that several specimens of aragonite and calcite differed from their museum labels.

Gypsum. For gypsum (monoclinic), it was necessary to show that the crystallographically different anhydrite (orthorhombic), often found in coal, and the hemihydrate (hexagonal, $CaSO_4 \cdot 1/2H_2O$), can be differentiated in the infrared for the preliminary qualitative analysis of the sample. Data from Morris (27) and from our laboratory, in Table 1 show that the hemihydrate has unique bands and can be differentiated from gypsum. These spectral differences were used to show that the low-temperature oxidation technique produced a conversion of gypsum to the hemihydrate. Gypsum was selected for testing in synthetic mixtures since it has been identified and analyzed in coal product samples not subjected to low-temperature ashing. Anhydrite is also readily distinguishable from gypsum. The primary difference is a splitting of the large, broad band of gypsum at 594 cm^{-1} into two sharp bands at 587 and 607 cm^{-1} for anhydrite. The 660 cm^{-1} band of

Table 1. - Infrared Absorption Bands for Minerals

Mineral	Absorption bands, cm^{-1} *
α-Quartz	256 (w), 360 (mw), 388 (mw), 452 (m), 465 (w, sh), 501 (mw), 688 (w), 772 (mw), 790 (m), 1075 (s), 1135 (w), 1160 (w)
α-Tridymite (synthetic) . .	465 (s), 500 (sh), 782 (m), 1088 (s), 1155 (sh)
α-Cristobalite**	485 (s), 515 (sh), 620 (m), 798 (m), 1104 (s), 1160 (sh), 1204 (w)
Calcite	217 (m), 337 (sh), 307 (s), 707 (m), 842 (vw), 869 (m), 1420 (s), 1600 (w), 1792 (vw)
Aragonite	205 (sh), 245 (s), 288 (sh), 692 (m), 705 (m), 836 (w), 850 (m), 1076 (w, sharp), 1450 (sh), 1464 (s), 1600 (w), 1780 (w)
Gypsum	215 (m), 298 (mw), 412 (w), 445 (w), 594 (m), 660 (m), 998 (vw), 1106 (s), 1132 (s), 1155 (s, sh), 1615 (m), 1680 (mw), 3250 (vw), 3400 (m), 3492 (sh, vw), 3550 (m)
Hemihydrate of $CaSO_4$. . . .	235 (m), 250 (sh), 412 (w), 455 (w), 590 (m), 605 (sh, w), 619 (w), 652 (m), 665 (sh, w), 1000 (mw, sharp), 1008 (vw, sh), 1090 (s), 1110 (s), 1128 (s), 1147 (s), 1613 (mw), 3552 (w), 3610 (mw)
Anhydrite	252 (m), 502 (vw), 587 (m), 606 (m), 669 (m), 875 (vw), 998 (vw), 1008 (vw), 1115 (s), 1148 (s)
Pyrite	284 (w), 340 (m), 391 (vw), 406 (s)
Marcasite	285 (w), 321 (m), 350 (m), 396 (s), 407 (s), 422 (vw)
Kaolinite	268 (m), 338 (m), 352 (vw, sh), 405 (vw, sh), 422 (m), 460 (s), 528 (s), 689 (m), 747 (w), 782 (w), 908 (s), 929 (w, sh), 1002 (s), 1026 (s), 1095 (s), 3622 (m), 3652 (w), 3670 (vw), 3698 (m)

* Very weak = vw; weak = w; medium = m; strong = s; shoulder = sh.
** Data from reference (21).

Table 2. - Analytical Absorption Bands and Absorptivities for Minerals

Mineral	Source	Absorption bands, cm^{-1} and absorptivities, 1/mm*
Quartz	Hot Springs, Ark. . . . . Rock crystal Ward's Natural Science Establishment, Inc.	360 (448), 388 (525), 452 (1010), 790 (589)
	Berkeley Springs, W. Va. . . Oriskany sandstone W. Va. University Geology Department	360 (430), 388 (500), 452 (970), 790 (580)
Calcite	Germany Valley, W. Va. . . Crystals W. Va. University Geology Department	307 (720), 869 (610), 1420 (2050)
Gypsum . . .	Niagara, N. Y. . . . . Crystals U. S. National Museum, No. 80022	594 (245), 660 (251)
	Washington County, Utah . . . Crystals Ward's Natural Science Establishment, Inc.	594 (246), 660 (254)
Pyrite	Park City, Utah . . . . . Ward's Natural Science Establishment, Inc.	340 (190), 406 (630)
	Gilman, Eagle County, ... Colo. Minerals Unlimited	340 (180), 406 (640)
Kaolinite . .	Macon, Ga., Oneal Pit . . . . API Reference Clay Mineral Kaolinite No. 4 Ward's Natural Science Establishment, Inc.	338 (353), 422 (505), 460 (986), 528 (1106), 689 (338), 747 (131), 908 (617)

* Absorptivities in parentheses.

gypsum shifts to 669 cm^{-1} in anhydrite, and the water vibrations appearing at 1615, 1680, 3400, and 3555 cm^{-1} are unique for gypsum. Data in Table 1 also show the differences between the hemihydrate and anhydrite.

Pyrite. Both polymorphs of FeS_2, pyrite and marcasite, have been identified in coal (6, 9, 36). White (37) has presented infrared data to 400 cm^{-1} which is insufficient for differentiation between these two polymorphs. However, the infrared spectra to 200 cm^{-1} obtained on samples in this laboratory show that these two polymorphs are distinguishable in this region. Table 1 shows that, although marcasite exhibits two bands common to pyrite, there are four distinctly different bands which uniquely characterize this polymorph. Further, the band at 340 cm^{-1}, which is unique for pyrite, allows detection of pyrite in marcasite samples. These infrared differences, along with X-ray confirmation, established the phase purity of the pyrite standards selected for calibration and thus also the qualitative identification of pyrite as the observed form occurring in the coal samples studied. It was particularly important to establish by X-ray that no pyrrhotite (FeS) was present in the standard samples since this mineral has no absorption in the entire 5000 to 200 cm^{-1} region. Optical examination is also often unreliable for this mineral class since out of 15 different mineral specimens labeled marcasite, two were pyrrhotite, six were pyrite, and only seven were actually marcasite as shown by infrared analysis.

Kaolinite. Clays other than kaolinite are found in coal. Kaolinite can be identified by infrared in mixtures of clay minerals and even in mixed-layer clay minerals (29). Montmorillonite, illite, and kaolinite predominate in many coals and Angino (4) has discussed the infrared spectral differences among these out to 90 cm^{-1}. The OH region is especially useful in the qualitative identification of kaolinite. Kodama (18) states that the absorption band at 3698 cm^{-1} can distinguish kaolinite from other clay minerals down to a few weight-percent of kaolinite in total amounts of clay minerals. Lyon (22) has shown that the use of ratios for bands appearing in the OH region, along with other spectral differences, enables a unique distinction to be made among the kaolin group minerals of kaolinite, dickite, and halloysite. This literature data, and data obtained in our laboratory from a number of API reference clay minerals, were used to substantiate the identification of kaolinite in the coal low-temperature ash samples and as a guide in the selection of bands for quantitative analysis.

Quantitative Analysis

The apparent absorptivity of a band was calculated from the relationship:

$$a = \frac{A}{b\,c}$$

where a = absorptivity in units of 1/mm;
A = absorbance of the band (baseline technique);
b = pellet thickness, mm;
c = concentration, weight-percent.

The value of absorptivity is specific for a 13 mm diameter pellet.

After completion of grind studies for each mineral, bands were selected for quantitative analysis. These selections were based on both their specificity and the constancy of their absorptivities with prolonged grinding. Table 2 lists the bands selected for analysis. When it is necessary, for the sake of specificity, to use a band which does not remain constant with particle size reduction beyond the minimum grind time, the error introduced must be considered.

Only one source for kaolinite was used for the calibration data because there is extensive mineralogical data for it in the literature. The data in Table 2 are the results of duplicate grind studies that were quite reproducible. Only one source of calcite was used because of the wide variation of absorptivity values from different sources, even though their spectra were qualitatively identical and their particle sizes were the same. Therefore, calcite from the same source was used for synthetic mixtures and for calibration data in order to obtain agreement. Additional work is required to resolve this limitation by examination of these samples by other analytical techniques in order to determine the cause for such a variation.

Several synthetic mixtures, listed in Table 3, were prepared to test the accuracy of the multicomponent analysis. Preground standard mineral samples of the required particle size were used and the same technique for pellet preparation used as described for the mineral standards. The concentration ranges of the pure minerals were selected to represent the concentration ranges commonly encountered in the coal samples examined. No attempt was made to determine the limit of detectability for each mineral since this was different for different sample compositions. Figure 3 shows the infrared spectrum of synthetic mixture No. 7, which approximated the composition of a typical coal low-temperature ash as shown in Figure 1, curve (c), except for the gypsum-hemihydrate conversion. When band overlapping occurred, the required absorbance correction was obtained from the standard spectra of the interfering mineral, using the standard procedures for quantitative analysis. An expedient technique of chart overlay to obtain background and band overlapping corrections was as accurate as the more time consuming procedure of matrix solution. The agreement shown in Table 3, within an average error of 6.2% for all minerals, demonstrates the method to be satisfactory for the multicomponent mixtures investigated. It is difficult, without an independent reliable method of analysis, to determine the accuracy limits of the infrared method when applied to coal ash samples. Greater accuracy is expected with the synthetic mixtures since they were prepared under controlled conditions of particle size and contained no unknown interferences. In our work it was necessary to pregrind coal samples to speed oxidation in the low-temperature asher. This pregrinding was sufficient to achieve the required particle size reduction for an accurate quantitative analysis, as ascertained by particle size measurements on the ash. Optimum particle size was also indicated for at least the mineral kaolinite from a grind study using its bands that appear fairly well resolved in the spectrum of the total coal sample (see Fig. 1). Grind curves similar to those in Figure 2 were obtained with a relatively small increase in absorptivity before becoming constant. It is essential to conduct a grind study on any mineral mixture prior to analysis in order to establish when the required particle size reduction for each component in the mixture has been achieved. The infrared analysis should be made only after absorptivity values have become constant and particle size has been checked.

Table 3. - Analysis of Synthetic Mixtures of Minerals

Synthetic mixture no.	Kaolinite, %		Quartz, %		Gypsum, %		Calcite, %		Pyrite, %	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
1	71.86	72.70	28.14	27.10						
2	69.60	71.15	30.40	29.13						
3	53.10	43.71	23.17	19.65	23.72	20.10				
4	41.53	41.04	19.29	19.33	39.18	33.50				
5	54.63	55.18	18.51	19.68	26.85	26.98				
6	29.92	29.39	12.50	11.53	47.32	48.10	10.26	10.31		
7	35.72	31.11	24.11	20.77	31.69	30.78	8.48	10.24		
8			12.21	14.22	33.07	31.13	12.20	12.40	42.52	44.92
9			22.90	19.00	31.30	31.20	8.40	7.00	37.40	30.00
10			15.20	12.00	30.50	30.80	10.60	11.30	43.00	35.12
Average error	2.6		1.9		1.7		0.8		5.9	

A limitation of the application of infrared spectroscopy to mineral mixtures in coal is in the analysis of pyrite in the presence of high amounts of kaolinite (15). Both of the analytical bands of pyrite are overlapped considerably by kaolinite bands and amounts of pyrite as high as 20% might be undetected when kaolinite is present to the extent of 30% or greater. For this reason, no attempt was made to analyze synthetic mixtures containing both. Work is continuing to develop a satisfactory analysis for kaolinite-pyrite mixtures when kaolinite content is high.

CONCLUSIONS

This paper describes the development of a quantitative infrared multicomponent analysis for five minerals commonly occurring in coal. It shows that a successful analysis for quartz, calcite, gypsum, pyrite, and kaolinite is possible if sampling conditions are controlled. The infrared region of 650 to 200 cm^{-1} is seen to contain data that contribute to both the preliminary qualitative and the quantitative analysis of these mixtures. The accuracy of the method was evaluated with tests on synthetic mixtures. Average errors were within 6.2% for all five component minerals. Although the method was primarily applied to the analysis of unaltered mineral matter obtained from coal by use of the new technique of low-temperature ashing in an oxygen plasma, the calibration data obtained can be used in the analysis of other materials connected with the mining and utilization of coal. For example, we have determined these minerals directly in coal mine refuse samples, which often have low organic matter content. The development of the analysis revealed that infrared spectroscopy is a valuable tool for differentiating among various polymorphic mineral forms and provides a collection of high resolution standard reference spectra for naturally occurring minerals and their polymorphs to 200 cm^{-1}.

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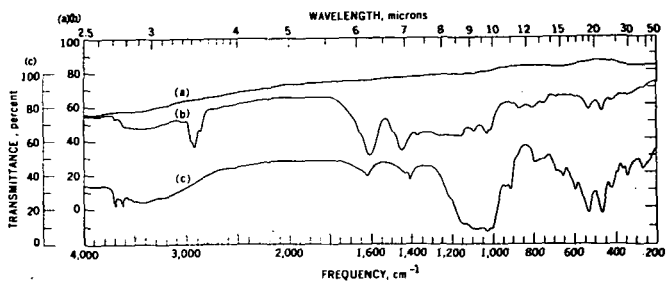

FIGURE 1. - Infrared Spectra of (a) Cesium Iodide, (b) Pittsburgh-seam Coal, and (c) Low-temperature Ash from Pittsburgh-seam Coal.

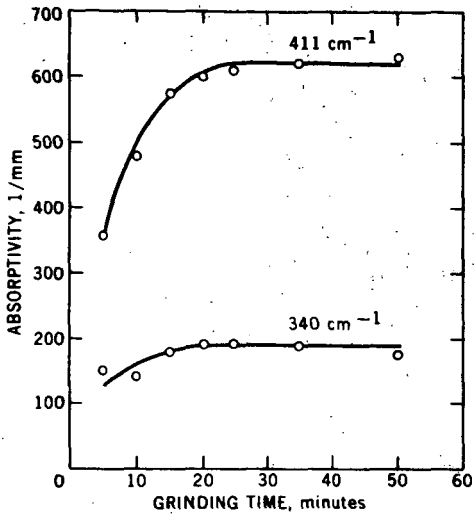

FIGURE 2. - Absorptivity as a Function of Grinding Time for Pyrite, in an Agate Vial.

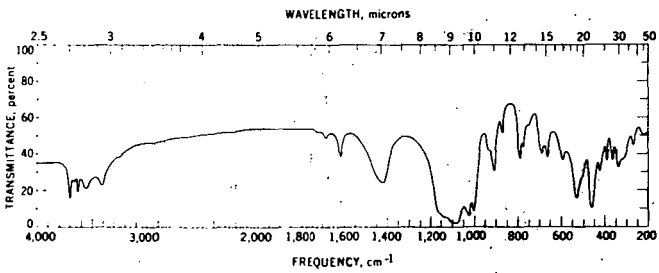

FIGURE 3. - Synthetic Mixture of Kaolinite, Calcite, Gypsum, and Quartz.